



Phase diagrams for aggregates of thick colloidal platelets



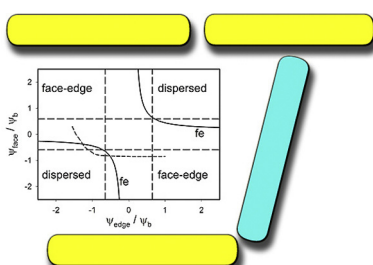
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HIGHLIGHTS

- We developed a micromechanical model for aggregated clay platelet configurations.
- We derived stability conditions for face–edge, face–face and edge–edge aggregates.
- The stability of face–edge aggregates depends on the surface curvature of edge walls.
- Phase diagrams for different clay aggregates have been constructed.
- The locations of kaolin gel phases appearing after rapid coagulation are predicted.

GRAPHICAL ABSTRACT



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ABSTRACT

The balance of van der Waals and electrostatic forces between the platelets in clay suspensions may lead to stable face–edge configurations. These configurations compete with face–face and edge–edge aggregates in clay gels. For clay platelets with thicknesses substantially larger than the interaction range, stability conditions for the different aggregates in terms of electric surface potentials, Debye-length, Hamaker constant and interface curvature in the edge region of the platelets are formulated. The stability conditions are useful to evaluate phase diagrams for mechanically and thermodynamically stable platelet aggregates.

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1. Introduction

Some clays such as kaolin consist of rather thick platelets with relatively low aspect ratios of about ten or twenty. These platelets are formed by a stack of many parallel sheets. Looking from above at the platelet surfaces, electron microscopic images and high resolution SEM micrographs often reveal polygons with straight sides, e.g. hexagons [1]. The diameter of a typical kaolinite platelet ranges between a half and a few micrometers, while its thickness

is between about fifty and a few hundred nanometers. The rheological properties of aqueous clay suspensions depend on many physical parameters such as volume density of the dispersed particles, particle shape and size, the pH value and the ionic strength of the electrolyte solution. Adjusting the pH and the ionic strength, sol–gel transitions can be enforced [2]. For colloidal suspensions the closest distance b between aggregated particles was estimated to be about 1 nm [3,4]. Based on fits of yield stress data of flocculated metal oxide suspensions Johnson et al. [5] found larger values for b , ranging between 2.3 and 2.6 nm, insensitive to particle size, volume fraction and pH for suspensions flocculated in the primary minimum [6]. The distance of closest approach of colloidal particles in water is substantially larger than the corresponding

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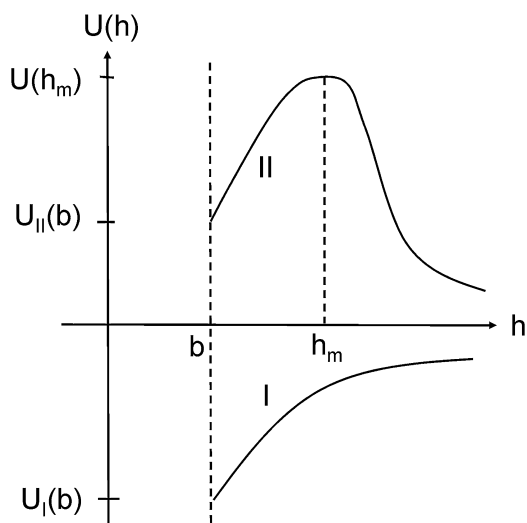


Fig. 1. Interaction potentials $U(h)$ of two colloidal particles at distances h slightly larger than the distance of closest approach b . The cases (I) and (II) accompanied with $U_I(b) < 0$ and $U_{II}(b) > 0$ lead to different stability conditions for platelet aggregates (Eqs. (41) and (42)).

distance of touching particles in vacuum. There exists the notion that strong short range repulsion forces prevent colloidal particles dispersed in water from approaching closer than a distance b . A reasonable assumption is that $b/2$ corresponds to a few immobile water layers adsorbed on each solid surface [2]. The value of b may be enhanced, if large ions surrounded by water shells or polymers are adhered to solid surfaces [6]. Avoiding a detailed description by a short range repulsion potential, the shortest possible particle distance b of aggregated particles may be introduced empirically in a similar way as for hard particle models in statistical thermodynamics [7]. Fig. 1 illustrates schematically two possible shapes of the particle–particle interaction potential for distances h close to the distance of closest approach b . In most cases the interaction potential for colloidal particles $U(h)$ satisfies the condition $U(b) < 0$. In this case the configuration of adhered gel particles is thermodynamically stable against peptization. If the pH value or the ionic strength of the aqueous dispersion agent is changed appropriately, the conditions $U(b) > 0$ and $[dU(h)/dh]_{h=b} > 0$ may be satisfied. Although, in this case, the interaction energy $U(h)$ does not have an absolute minimum for $h = b$, peptization of a gel could be avoided, when the potential barrier $\Delta U = U(h_m) - U_{II}(b)$ against rupture of particle junctions is sufficiently high (Fig. 1). Actually, in most cases the thermal kinetic energy associated with Brownian translational motion is considerably lower than the large energy barrier needed to break the linkage between coagulated colloidal particles. As will be demonstrated in this paper, the cases $U(b) < 0$ (I) and $U(b) > 0$ (II) should be distinguished for assessing the stability of different orientations of adhered anisometric colloidal particles. If the conditions $U(b) > 0$ and $[dU(h)/dh]_{h=b} > 0$ are satisfied a gel consisting of coagulated aggregates is mechanically stable, but not thermodynamically stable against a slow transformation into a sol. Apart from $[dU(h)/dh]_{h=b} > 0$, thermodynamic stability against a slow peptization of a gel requires that the additional condition $U(b) < 0$ holds.

Clay particles have different electric charge densities at platelet faces and edges. Kaolinite platelets are known to have several favored aggregated configurations depending on the electric surface charge distribution. If the charge density of the platelet faces is zero or low, a band-like structure similar to overlapping coins can be stable [8]. This arrangement competes with the house-of-cards structure, where neighboring platelets are perpendicular to each other and edges are adhered to faces. A house-of-cards structure is

supposed to be favored if edges and faces are oppositely charged. In a third aggregated structure edges are adhered to edges. Such aggregates may occur, if the pH value of the aqueous solution is adjusted close to the isoelectric point of the edges, where the electric surface potential (zeta potential) of edge regions vanishes. If the edges of clay platelets adhere to each other, the density of the solid gel skeleton is lower than gel skeleton densities resulting from face–face or face–edge aggregations [9]. Hence, several structurally different gel phases may occur. A gel with T-shaped junctions, the house-of-cards structure, could have other rheological properties than a gel with predominantly parallel platelets.

Unfortunately, the construction of phase diagrams that contain the dispersed state and several gel structures is often hampered by hysteresis effects, when the final state depends on details of the sample preparation and the chosen path from an initial state. However, conditions for mechanical stability can impose restrictions on aggregated structures. Configurations which are mechanically unstable are hardly observable, because they should decay relatively fast. According to the DLVO-theory the interaction between clay platelets mainly comprises van der Waals and electrostatic forces [10]. The electrostatic forces can be evaluated by the Poisson–Boltzmann theory. The boundary conditions used for evaluating the electrostatic potential must be chosen appropriately in accord with experimental observations. In most cases either a constant electric potential or a fixed surface charge is imposed as the boundary condition for solid/water interfaces. In the case of clay platelets, however, different boundary conditions for face and edge regions were postulated. Furthermore, minerals classified as 1:1 clays should have different faces. For example, a thick kaolinite particle can be considered as a stack of many layers, where each layer has an alumina and a silica surface. Nevertheless, many authors assumed that both kaolinite platelet faces have a fixed negative electric charge density, whereas edge regions have a constant electric potential at fixed pH value of the aqueous solution [11]. However, recent AFM-investigations query this traditional picture and suggest that the boundary conditions for both faces of a kaolinite platelet differ considerably from each other [12,9]. It could be possible that one face of kaolinite platelets (silica face) has a constant permanent charge, whereas the boundary condition for the other face (alumina face) is better described by assuming a constant electrostatic potential. On the other hand, kaolinite particles with two identical surfaces were found as a consequence of a layer inversion within the layer stack that forms a particle [13]. It is also possible that clay platelets are bound together by other clay materials causing both exposed particle surfaces to be silica surfaces [14]. Since conclusive evidence for an appropriate choice of the boundary conditions is still lacking, several combinations of electrostatic boundary conditions should be taken into account.

In this paper, we formulate conditions for mechanical stability of aggregates consisting of plate-like particles with rounded edge regions. Face–edge, face–face and edge–edge aggregates are considered. The stability of these platelet configurations depends on zeta potentials of the face and edge regions, the Debye length or electrolyte concentration, the Hamaker constant and the distance of closest approach between aggregated particles. If the interaction range is sufficiently small in comparison to particle size and curvature radii, Derjaguin’s approximation allows us to evaluate pair potentials, forces and torques for aggregates of heterocoagulated particles. For checking the accuracy of the mathematical procedure, approximated results for the effective platelet–platelet pair potential and its derivatives are compared with the results of a numerical procedure that dispenses with Derjaguin’s method. Finally, phase diagrams for the favored aggregates which are formed by rapid coagulation from the dispersed state are evaluated and discussed.

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